

## Claims

1. A process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, which comprises:

adding, to a water solvent, resorcinol (A) in an amount of 20 to 150 parts by weight relative to 100 parts by weight of water, an inorganic salt (B) in an amount of 20 to 80 parts by weight relative to 100 parts by weight of water, and an organic solvent (C) having a solubility parameter of 7.0 to 12.5 and capable of dissolving the resorcinol-formalin resin in an amount of 10 to 200 parts by weight relative to 100 parts by weight of resorcinol (A);

stirring the mixture at a liquid temperature not higher than the boiling point of the organic solvent (C) to give a two-phase system containing no remaining solid matter;

adding a catalytic amount of an organic acid or inorganic acid (D);

adding 1 to 40% formalin (E) dropwise in a molar

ratio of formaldehyde/resorcinol of 0.3 to 0.8 under stirring over a period of 1 to 300 minutes while maintaining the reaction system at 0 to 60°C;

stirring the mixture for further 10 to 60 minutes after the completion of the dropwise addition to cause a liquid-liquid heterogeneous reaction to proceed;

allowing the reaction system to stand while maintaining it at the temperature of the reaction to separate it into two layers;

removing the aqueous layer;

adding an organic solvent (C) in an amount of 1 to 5 equivalents to the amount of the reaction product to the reaction product layer which is an organic solvent layer to effect dilution;

adding water to the reaction product layer in an amount which is half of the amount of the organic solvent;

stirring the reaction system while maintaining its temperature to be not higher than the boiling point;

separating it into two layers after allowing it to stand; and then

removing the aqueous layer to obtain a resorcinol-formalin resin.

## 2. The process for producing a resorcinol-

formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to claim 1, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the 1 to 40% formalin (E) is intermittently added dropwise in a molar ratio of formaldehyde/resorcinol of 0.3 to 0.8 under stirring over a period of 20 to 300 minutes.

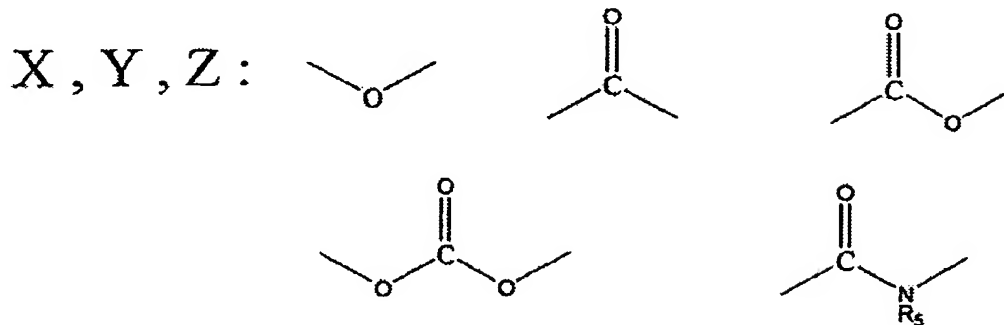
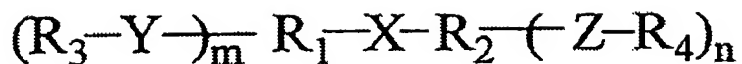
3. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 2, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein a peak area corresponding to the resorcinol pentanuclear or higher nuclear bodies is from 30% to 55% relative to the whole peak area and a peak area corresponding to the resorcinol monomer is from 3% to 9% relative to the whole peak area, the peak areas being obtained by gel permeation chromatographic analysis of the above resorcinol-formalin

resin.

4. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 3, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the organic solvent (C) is an organic solvent having a solubility parameter of 9.0 to 11.0.

5. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 4, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the organic solvent (C) is an organic solvent represented by the following general formula [1]:

General formula [1]



wherein m represents 0 or 1, n represents 0 or 1, and  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ , and  $R_5$  each independently represents a methyl group, an ethyl group, an n-propyl group, a 2-propyl group, an n-butyl group, a secondary butyl group, an isobutyl group, or a tertiary butyl group;  $R_1$  and  $R_2$  may be combined to form a ring when  $m=n=0$ ,  $R_2$  and  $R_3$  may be combined to form a ring when  $m=1$  and  $n=0$ , and  $R_3$  and  $R_4$  may be combined to form a ring when  $m=n=1$ .

6. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 5, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the organic

solvent (C) is used as a mixture of two or more thereof.

7. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 6, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the inorganic salt (B) is a salt formed from one or two or more cations selected from alkali metals and alkaline earth metals and one or two or more anions selected from a sulfate ion, a nitrate ion, a chlorine ion, a bromine ion, an iodine ion, and a thiocyanate ion.

8. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 7, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the inorganic salt (B) is calcium chloride.

9. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 8, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the amount of the organic solvent (C) added is from 30 to 100 parts by weight relative to 100 parts by weight of resorcinol (A).

10. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 9, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the organic acid or inorganic acid (D) is hydrochloric acid.

11. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced

content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 10, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the mole number of formaldehyde in the formalin (E) relative to the mole number of resorcinol (A) is in a molar ratio of formaldehyde/resorcinol of 0.5 to 0.8.

12. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 11, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein time for the dropwise addition of the formalin (E) is from 20 to 120 minutes.

13. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any



one of claims 1 to 12, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein water is added in an amount of 1 to 10 equivalents by weight to the resorcinol-formalin resin in the organic solvent (C) solution of the resorcinol-formalin resin and the organic solvent (C) is removed by distillation to finally obtain an aqueous resorcinol-formalin resin solution having a reaction product concentration of 30 to 80% and a moderate flowability.

14. The process for producing a resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies according to any one of claims 1 to 12, the whole steps including an one-stage reaction and liquid-liquid distribution being conducted in the same reactor, wherein the organic solvent (C) is added to the organic solvent layer obtained by the separation into two layers after allowing to stand and the removal of the aqueous layer, in an amount of 2 to 10 equivalents to the weight of the reaction product to effect dilution, water is removed by distillation at the azeotropic temperature of water and

the organic solvent, and then solid matter is removed by filtration after cooling to room temperature.

15. A resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, the process comprising:

adding, to a water solvent, resorcinol (A) in an amount of 20 to 150 parts by weight relative to 100 parts by weight of water, an inorganic salt (B) in an amount of 20 to 80 parts by weight relative to 100 parts by weight of water, and an organic solvent (C) having a solubility parameter of 7.0 to 12.5 and capable of dissolving the resorcinol-formalin resin in an amount of 10 to 200 parts by weight relative to 100 parts by weight of resorcinol (A);

stirring the mixture at a liquid temperature not higher than the boiling point of the organic solvent (C) to give a two-phase system containing no remaining solid matter;

adding a catalytic amount of an organic acid or

inorganic acid (D) ;

adding 1 to 40% formalin (E) dropwise in a molar ratio of formaldehyde/resorcinol of 0.3 to 0.8 under stirring over a period of 1 to 300 minutes while maintaining the reaction system at 0 to 60°C;

stirring the mixture for further 10 to 60 minutes after the completion of the dropwise addition to cause a liquid-liquid heterogeneous reaction to proceed;

allowing the reaction system to stand while maintaining it at the temperature of the reaction to separate it into two layers;

removing the aqueous layer;

adding an organic solvent (C) in an amount of 1 to 5 equivalents to the amount of the reaction product to the reaction product layer which is an organic solvent layer to effect dilution;

adding water to the reaction-product layer in an amount which is half of the amount of the organic solvent;

stirring the reaction system while maintaining its temperature to be not higher than the boiling point;

separating it into two layers after allowing it to stand; and then

removing the aqueous layer to obtain a resorcinol-formalin resin.

16. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, according to claim 15, wherein the 1 to 40% formalin (E) is intermittently added dropwise in a molar ratio of formaldehyde/resorcinol of 0.3 to 0.8 under stirring over a period of 20 to 300 minutes.

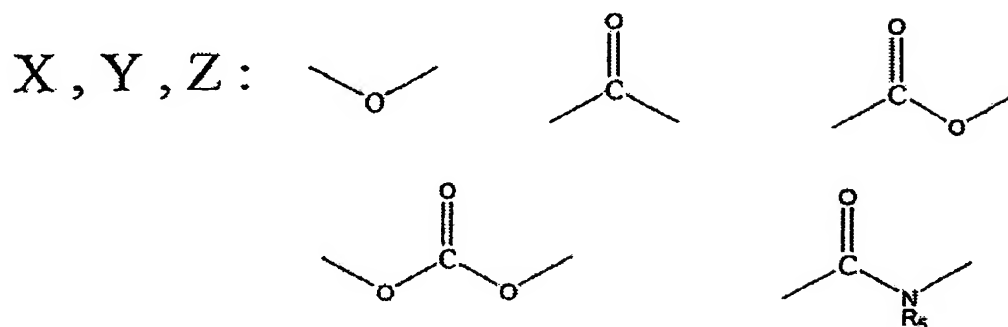
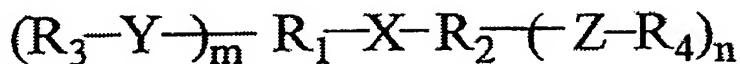
17. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, according to any one of claims 15 to 16, wherein a peak area corresponding to the resorcinol pentanuclear or higher nuclear bodies is from 30% to 55% relative to the whole peak area and a peak area corresponding to the resorcinol monomer is from 3% to 9% relative to the whole

peak area, the peak areas being obtained by gel permeation chromatographic analysis of the resorcinol-formalin resin.

18. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, according to any one of claims 15 to 17, wherein the organic solvent (C) is an organic solvent having a solubility parameter of 9.0 to 11.0.

19. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, according to any one of claims 15 to 18, wherein the organic solvent (C) is an organic solvent represented by the following general formula [1]:

General formula [1]



wherein m represents 0 or 1, n represents 0 or 1, and  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ , and  $R_5$  each independently represents a methyl group, an ethyl group, an n-propyl group, a 2-propyl group, an n-butyl group, a secondary butyl group, an isobutyl group, or a tertiary butyl group;  $R_1$  and  $R_2$  may be combined to form a ring when  $m=n=0$ ,  $R_2$  and  $R_3$  may be combined to form a ring when  $m=1$  and  $n=0$ , and  $R_3$  and  $R_4$  may be combined to form a ring when  $m=n=1$ .

20. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and

liquid-liquid distribution are conducted in the same reactor, according to any one of claims 15 to 19, wherein the organic solvent (C) is used as a mixture of two or more thereof.

21. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, according to any one of claims 15 to 20, wherein water is added in an amount of 1 to 10 equivalents by weight to the resorcinol-formalin resin in the organic solvent (C) solution of the resorcinol-formalin resin and the organic solvent (C) is removed by distillation to finally obtain an aqueous resorcinol-formalin resin solution having a reaction product concentration of 30 to 80% and a moderate flowability.

22. The resorcinol-formalin resin containing no inorganic salts and having a reduced content of resorcinol monomer and a reduced content of resorcinol-formalin resin of resorcinol pentanuclear or higher

nuclear bodies, produced by a production process where the whole steps including an one-stage reaction and liquid-liquid distribution are conducted in the same reactor, according to any one of claims 15 to 20, wherein the organic solvent (C) is added to the organic solvent layer obtained by the separation into two layers after allowing to stand and the removal of the aqueous layer, in an amount of 2 to 10 equivalents to the weight of the reaction product to effect dilution, water is removed by distillation at the azeotropic temperature of water and the organic solvent, and then solid matter is removed by filtration after cooling to room temperature.